NON-UNIFORMITIES IN HYDROGEN AND OXYGEN CONCENTRATION IN NIOBIUM FILMS

W.R. Frisken, Physics and Astronomy, York University, Toronto ON M3J 1P3, Canada, and
L.N. Hand, Physics Dept., and Cornell Center for Materials Science, Cornell, Ithaca NY 14853, USA.

Abstract

This note gives a first look at non-uniformities in the volume distribution of light element impurities in sputtered niobium films. The film reported here is 2000 nm. niobium on an MgO substrate, capped with 200 nm. of titanium. We find evidence for a corrosion mechanism involving the initial penetration of the film by hydrogen, followed by oxygen. Possible implications of this for superconducting radio frequency cavities are discussed.

1 BACKGROUND

There are several high energy accelerator installations using superconducting radio frequency (SRF) cavities [1,2]. Some (CEBAF, KEK, TTF) forge and weld their cavities from Niobium sheet 2 mm thick, but LEP at CERN uses copper cavities plated inside with a 1.5 micron thick film of niobium. (The RF fields penetrate only the first few hundred nanometers of the superconductor). There is much engineering lore associated with the handling and "conditioning" of SRF cavities.

Impurities interfere with the RF superconductivity of niobium, and limit the performance of both "bulk" niobium cavities and "sputter-coated" niobium film cavities.

Hydrogen content influences both the linear and non-linear residual resistance of both bulk niobium cavities and sputter-coated copper cavities. The presence of hydrogen in the niobium in particular is known to be associated with a non-linearity called the "Q-disease" in which the residual surface resistance increases with impressed field, so that the cavity's Q (quality factor) diminishes progressively as the cavity is run at higher and higher voltage. Bonin and Roeth [3] review the experience with bulk cavities, and find a model with a uniform surface layer of hydride to have rather "far fetched" phase transitions, and a competitor with "hydride islands" to provide insufficient surface resistance. The CERN group [4] experience shows the detailed behaviour of hydrogen's influence on surface resistance in sputter-coated cavities to be tempered by the existence of an oxide layer on the substrate before sputtering.

Niobium is a getter [5]. It dissolves and traps gases like hydrogen and oxygen, and also other light elements like carbon, and nitrogen. Titanium is a better getter, and can be made to clean light element impurities out of niobium by heating the two metals together in a vacuum furnace [6].

SRF cavities are known often to fail locally rather than globally, and to fail in the same spot repeatedly [7]. The site of failure is located by high precision temperature mapping over the cavity surface, whereafter a piece of the cavity wall can be cut out and subjected to careful analysis by several techniques. Sites of failure due to the presence of large implants (e.g. tantalum, from poor rolling mill control) or metallic impurity concentrations at the end of a weld have been identified. However, the cause of failure, even when it occurs repeatedly at the same site, is not always evident. Often the failure must be assigned to "thermal breakdown", a term used in the field to mean "cause or causes unknown".

If the impurity is a gas like hydrogen, once the cavity has failed and been restored to room temperature, and especially if the engineering staff has tried to "power process" the cavity [8], the site of failure has been subject to temperature excursion, and there is little chance to investigate further. The question arises whether a gas like hydrogen is distributed interstitially and uniformly throughout the niobium superconductor, or whether it can exhibit regions of local concentration, which could be normal conducting hydrides and thus possibly contribute to thermal breakdown.

2 THE PRESENT WORK

The present work is part of a program to investigate the typical light element content of niobium films magnetron sputter-coated onto MgO and sapphire (Al_2O_3) single crystal substrates. The first films have been argon sputtered in a vacuum of 10-6 Torr, i.e. under industrial rather than UHV lab conditions. About 10% of their thickness consists of an added layer of titanium, either pre-sputtered onto the substrate, or post-sputtered onto the exposed surface of the niobium. All films were produced in the Technical Operations Facility of the Cornell Center For Materials Research (CCMR) in Clark Hall at Cornell.

We investigated the resultant films by several surface (and subsurface) investigation techniques, RRR (Residual Resistance Ratio), XRD (X-Ray Diffraction), EDS (Energy Dispersive Spectroscopy) and AFM (Atomic Force Microscopy). The relevant data on the films discussed here are summarized in the Appendix.

We have recently begun to study the spatial distribution of light elements in films deposited on the MgO substrate, using Secondary Ion Mass Spectroscopy (SIMS) technology. The facility for this investigation was provided by Professor Stewart McIntyre and his associates in the Surface Science Western (SSW) laboratories at the University of Western Ontario.

We present preliminary concentration distributions for a film of 2000 nanometers of niobium on MgO substrate, capped with 200 nanometers of titanium. As part of a broader program, this sample had been heat treated at Cornell to 600 C in a vacuum of 10^{-6} Torr for 30 minutes.

For these runs SSW's SIMS spectrometer used a focused cesium ion beam to etch the surface away, digging a crater as it rastered over a surface 250 microns square. Secondary ions emitted from the exposed surface were received by the mass spectrometer and recorded as a function of time, not only crater etching time (yielding the depth Z), but also raster sweep phase (yielding the lateral positions X,Y). This allowed the spectrometer to collect and record concentration data in two modes, a depth profiling mode, and a three dimensional imaging mode [9].

Depth Profiles of Concentration: In its simplest mode the spectrometer measured a concentration profile as a function of depth. In this mode the secondary ions of a specified mass received from the central 60 micron diameter region in the bottom of the crater were integrated and recorded periodically as the crater depth increased. Profiles were taken for hydrogen, carbon, oxygen, titanium and niobium during the etching of a single crater, and in all six such multiple depth profile craters were etched through this film.

3-D Image Distributions: the spectrometer could also measure and display an areal image for each selected element at each of a sequence of depths in the film, thus providing lateral as well as depth information. The finite spatial resolution in depth due to the plural scattering physical basis of the secondary emission process was about 10 nanometers, while the lateral resolution due to primary beam size was about 1 micron. Three runs recording 3-dimensional distributions were made for both the hydrogen and oxygen concentration.

Figure 1 shows a typical vertical profile. The niobium has invaded the titanium layer. Most of the concentrations appear to go to zero or become erratic in the MgO. This appearance is an artifact of the basic process, as the exposed MgO (an electrical insulator) becomes charged up by the primary cesium ion beam, whose thus reduced incident energy is insufficient to cause secondary emission. Note that no corrections have been made for the expected variation of secondary emission efficiency with base material. This variation can be quite marked, especially for massive ions like Nb, leading to the erroneous impression that there is more niobium in the titanium layer than in the niobium itself.

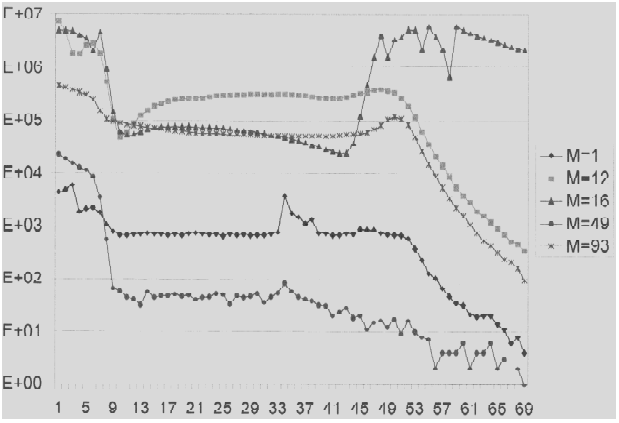

Figure 1: SIMS profiles of H, C, O, Ti and Nb in a heat treated film of 2000 nm. Niobium, magnetron sputtered onto a MgO substrate, then capped by a 200 nm. layer of Titanium. Depth steps are approximately 30 nm.

The figure indicates "gettering" of the light elements by the titanium layer during the heat treatment, but also some evidence that the niobium has reduced the MgO, making it an unintended source of oxygen near to the substrate depth. This may have happened during the sputtering operation, and will be the subject of further study.

The hydrogen profile shows a bump in the concentration more than 100 nm. deep. This type of feature is typical of our other hydrogen profiles, which exhibit similar bumps but at unrelated depths, suggesting lumps rather than layers of hydrogen concentration. It was this feature which led us to make the areal maps to get the 3-D picture.

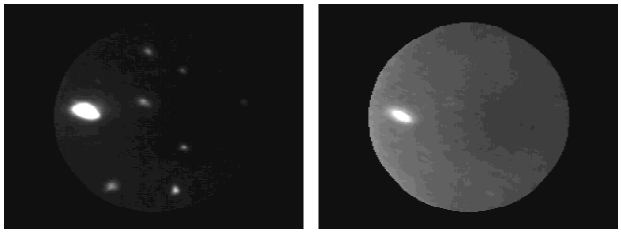

Figure 2: SIMS areal images of Hydrogen (left image) and Oxygen (right image) distributions from a 150 micron diameter field on a subsurface layer midway through the film's Titanium cap layer.

Figure 2 shows typical areal images for hydrogen and oxygen at the third depth, midway through the titanium layer. They exhibit several very marked local concentrations of hydrogen, the brightest (at 9 o'clock) being spatially coincident with a local concentration of oxygen. Comparing images taken in a sequence of neighbouring depths shows these bright spots to be sections through columns of hydrogen, and in the above noted instance, oxygen. In addition, within the cap layer of titanium there is a visible uniform distribution of oxygen, which disappears at the titanium-niobium interface. A similar but stronger oxygen feature occurs in the last 20% of the niobium layer, adjacent to the MgO substrate.

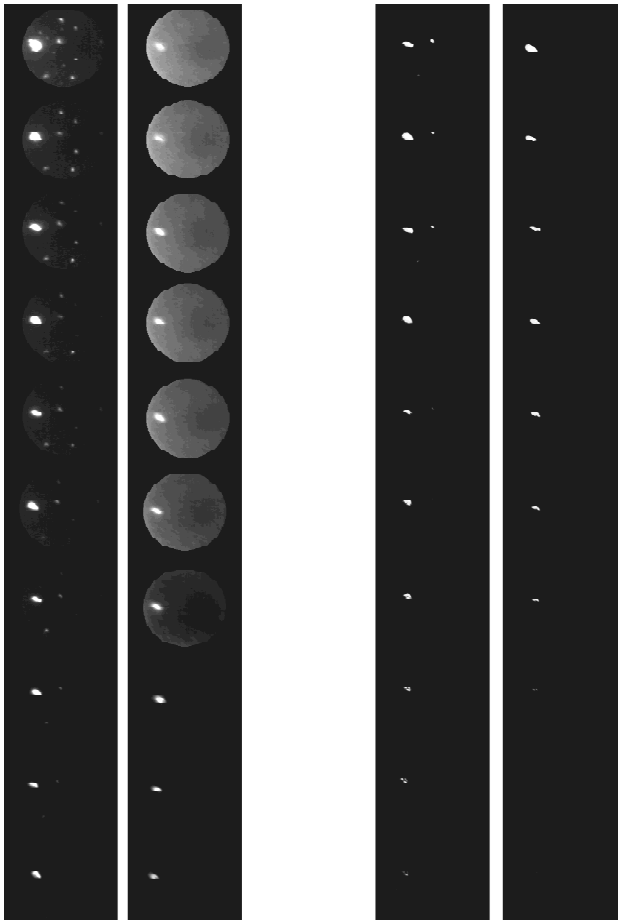

Figure 3A: Pairs of 150 micron diameter SIMS images for hydrogen and oxygen every 30 nm in depth as surface is etched away. Left column of pairs are the first 10 depths sampled, right column is the next 10. Image pair on upper left is at the top of the Ti cap layer, and the pair on the lower right is deep in the niobium film. The Ti-Nb interface is at about the 7th layer. The contrast and brightness has been enhanced in the image pairs at depths 11 to 20, to give increased sensitivity at greater depth.

Figures 3A and 3B show that most of the columns of hydrogen dry up before reaching the niobium layer. However, once we get through the impurity rich titanium cap layer, we can lower the detection threshold and track the brightest of them all the way through to the MgO substrate: two tiny bright spots appear at 9 o'clock in the hydrogen image at every depth until the MgO substrate is reached. Moreover, a 9 o'clock bright spot in the corresponding oxygen images is seen to accompany this brightest hydrogen spot as far as the 18th depth, yielding a column of hydrogen/oxygen which penetrates deep into the niobium film. At depth 43 (towards the bottom of column 4 of Figure 3B) the oxygen component reappears, and builds up strongly as the substrate is approached.

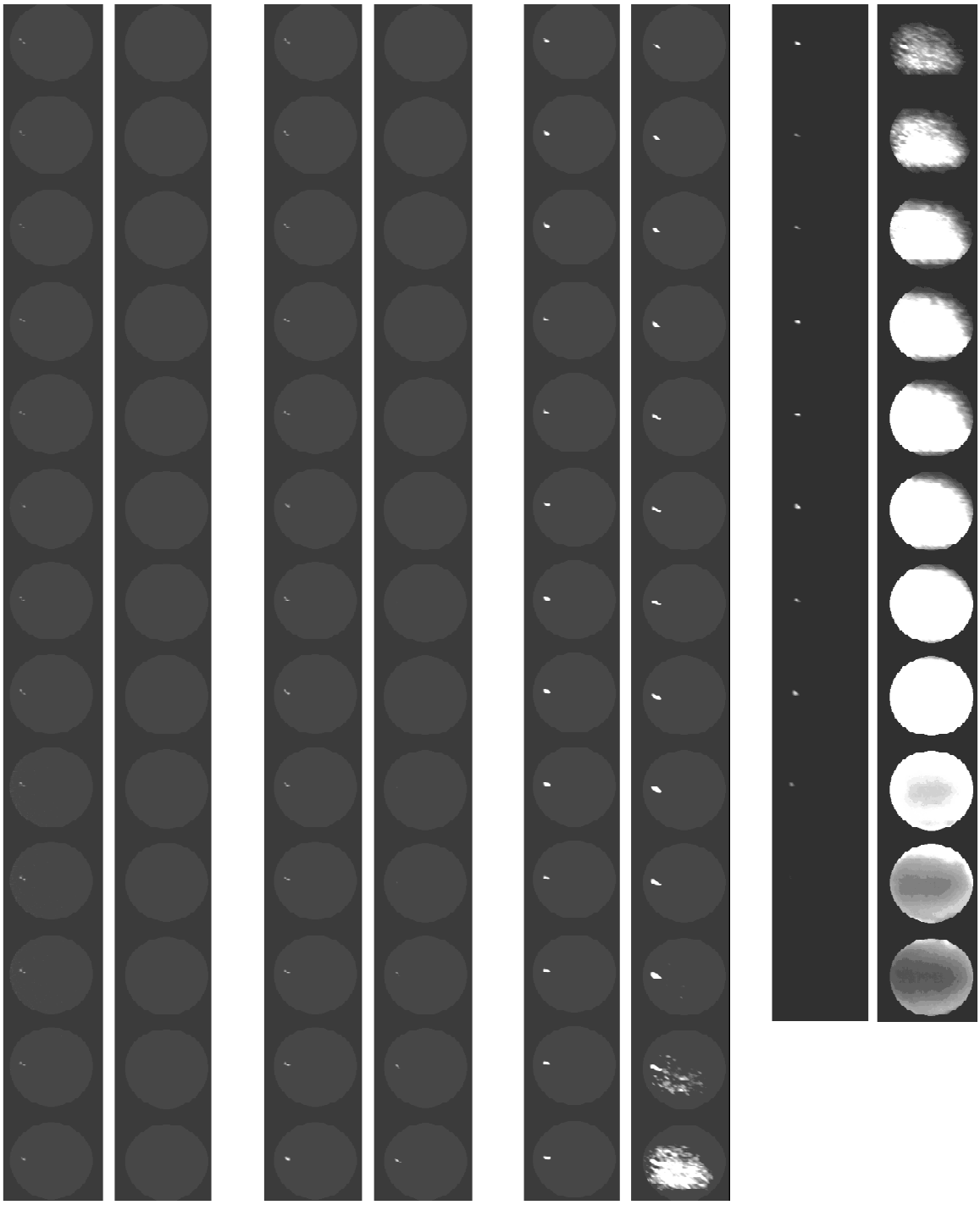

Figure 3B: Pairs of 150 micron diameter hydrogen and oxygen SIMS images as in Figure 3A, but for layers 21 (partway through the Nb layer, upper left) through 70 (entering the insulating substrate, lower right). The brightness and contrast is enhanced for the image pairs in the low noise region away from the substrate (layers 21 through 59).

The images of the last 10 depths nearest the substrate show a much larger, widely dispersed "flare" of oxygen, starting in the images at the bottom of column 6 in Figure 3B. This indicates a fairly uniform reservoir of oxygen-rich niobium at the very bottom, next to the substrate. The hydrogen column goes right through this reservoir region until it reaches the substrate. Its companion column of oxygen can be followed into the reservoir, but it is eventually lost in it.

These images show that hydrogen tends to form in columns. They also suggest that such a column of hydrogen may provide a channel for the subsequent absorption of oxygen from the surface (or from some other reservoir), and its associated migration deep into the body of the metal. Some of these changes may have occurred at room temperature.

These data open many questions, and demand further research.

Were the hydrogen columns formed after the heat treatment? Surely this structure could not have survived 30 minutes at 600 C. After heat treatment the samples were closed in individual plastic boxes, kept in Dryerite [10] in a larger plastic box for several weeks.

How much of the oxygen which moves up from below actually came from the reduction of the substrate? Although the free energies of NbO and MgO indicate that Nb cannot reduce MgO chemically, the sputtering process is not an equilibrium situation, and the Nb atoms arrive with sufficient kinetic energy to do this. We can put a limit on the extent of this effect from our surface resistivity measurements: no more than 4 nm. of the MgO surface could be reduced in this way.

Why are the rivers so precisely vertical? Why are they continuous from the titanium through to the niobium? Any pinhole in the niobium is unlikely to also occur in the titanium, as the films were sputtered separately. The niobium and titanium grains grow normal to the substrate---columnar growth. Does the hydrogen (and the oxygen) move preferentially through the lattice of single crystal grains? Clusters of grains? (The hydrogen/oxygen column is a few microns wide, and our grain size is typically 100 nm. However the lateral spatial resolution of the SIMS is on the order of a micron, so our grain boundaries cannot be resolved.)

Oxygen is known to bind hydrogen strongly in niobium [5]. Are we looking at a corrosion mechanism (see McIntyre et al [9] re zirconium)? It seems important to determine whether this is a universal corrosion mechanism, common to all niobium and titanium films, and perhaps to other metals. By subsequent more recent measurements, not reported here, we found that such columns of hydrogen and oxygen form under similar conditions in a bare niobium film, that is one with no titanium cap layer.

Our spatial resolution and sensitivity to hydrogen and oxygen limit us to columns on the order of one micron wide or wider. We do see a distribution of sizes on this scale. Do much smaller columns exist which are more numerous, but not resolved with our present technique?

The absence of lateral hydrogen diffusion away from the columns means that they are probably in the beta hydride phase, rather than in the freely diffusing alpha phase [11]. Since the beta phase is known not to be a superconductor, what are the implications of these oxygen/hydrogen columns for losses in superconducting RF cavities? Could they contribute to the RF residual resistance at very low temperatures? Would a hydrogen/oxygen column cause a "thermal breakdown" in a cavity? What non-linearities would higher RF fields produce? Could the hydrogen/oxygen migrate laterally, and the columns coalesce? Would any uniformly distributed oxygen and hydrogen migrate laterally, and coalesce into columns under intense RF excitation? Of particular importance is the question whether hydrogen/oxygen columns could serve as crystallization centers for hydrogen in the beta phase at very low temperatures. Perhaps the "hydride islands" model will need to be revisited after further experimental work.

3 ACKNOWLEDGEMENTS

We thank Professor Karl Berkelman and Professor Hasan Padamsee of the Cornell Laboratory of Nuclear Studies for making available the laboratory space and liquid helium for the RRR measurements. Dr. Maura Weathers of the X-ray diffraction lab at Cornell performed the x-ray measurements. Dr. John Hunt of CCMR made the EDS measurements. Gerhard Schmidt of the CCMR made the films and Ron Kemp, also of CCMR, ran the vacuum furnace.

We thank Professor Stewart McIntyre, Director of Surface Science Western and Professor of Chemistry at the University of Western Ontario for the use of his SIMS spectrometer, and Research Scientist on the SSW staff, Cindy Huctwith for making the measurements.

The Cornell Center for Materials Research is supported by the U.S. National Science Foundation.

One of us (W.R.F) wishes to thank York University for funds granted for his research as Senior Scholar, and as Walter Gordon Research Fellow.

4 APPENDIX: FILM DETAILS

In this appendix we give the results of various measurements on the film reported above. This film was subjected to a heat treatment at 600 C in a vacuum furnace for one half hour. For comparison, we will also list the results of measurements on a similar film which was not

heated. The purpose of the heat treatment was to observe possible gettering of oxygen from the niobium part of the film by the titanium, which was in intimate contact with it.

For the purposed of identification, these films are designated "I-Ti/Nb-R" (not heated) and "I-Ti/Nb-S" (heat treatment). The latter film is the one reported in the SIMS measurements in the body of this report above. The films will be known as "R" and "S" henceforth in what follows. The "R" film is intended only for comparison.

The niobium film was sputtered onto the magnesium oxide substrate crystal with a substrate temperature of 600 C, the titanium cap layer was then added with the Niobium film and substrate at room temperature.

It is rather surprising that the niobium alloyed itself with the titanium at the rather low treatment temperature of 600 C and in the short time of one half hour. The calculated diffusion distance of oxygen in niobium at this temperature and for this time is 24 microns (rms), and in β-titanium, 16.4 microns. This means that the ideal heating time could perhaps have been less than five minutes. We were limited by the furnace to a rather longer time, however. Furthermore, the titanium is initially α-titanium, which has a much lower oxygen diffusion constant (about 1/2 micron). When alloyed with niobium, the structure changes to a β structure, with consequent faster diffusion. We expect very little diffusion of titanium into niobium [12]. This is consistent with the experimental SIMS results, and what has been seen on other samples. We do not see the formation of Ti/Nb alloy at 500 C.

X-ray diffraction measurements show that there was no trace of an α phase in the heated film (S), while this phase is clearly visible in the unheated film (R). In a separate experiment on another film, the XRD results indicate the α-Ti phase still remains if the furnace temperature is only 500 C. The α–> β transition temperature of pure titanium is 886 C, so the presence of the niobium has a strong influence on this transition.

The ratio (RRR) of the resistivity of these films at room temperature to the resistivity at just above the superconducting transition temperature (about 10 K) was measured. From these measurements, we can extract a residual resistivity ρ_0. From the room temperature resistivity, we can calculate a film thickness if we assume a nominal value for the resistivity. The results for these films are given in Table 1.

Table 1: Film Characteristics

Film	**RRR** (Measured)	ρ_0 (μohm-cm)	**Calculated Film Thickness** (microns)
R	6.1 (.1)	2.78	1.70
S	13 (1)	1.20	1.89

The heat treatment gettering appears to have improved the RRR by a factor of two. The films could have varied in thickness enough to account for the discrepancy in the last column. Addition of a titanium cap layer should be only a 3% effect at room temperature. The film "S" has the highest value of RRR we have ever measured.

Although our SIMS measurements have not yet been calibrated to give quantitative concentration information, an oxygen + carbon + nitrogen impurity content of 1000 PPM (atomic fraction) would contribute approximately 0.5 μohm-cm to ρ_0. We have found the rest tends to come mainly from grain boundary scattering, which is expected to dominate the residual resistivity for thin films.

The EDS analysis, using X-rays excited by KeV electrons, confirmed the lack of heavy element impurities in the niobium part of the film. We typically find the chief impurity to be about 400 PPM of tantalum. It also showed no trace (less than .04 wt %) of argon in film "S", in contrast with other films we have sputtered with lower substrate temperatures. The EDS was not sensitive to the presence of light elements in trace amounts.

Figure 4 shows a contact AFM picture of the (oxidized) surface of a bare niobium film (no Ti cap layer) prepared in the same series as "S". Since the films were exposed to air between deposition of the niobium and the titanium, "S" was oxidized too. An oxygen layer at the Ti/Nb interface shows up in SIMS depth profiles of unheated films, but is not evident in Figure 1 because "S" 's oxide layer was dissolved during heat treatment.

The AFM picture covers an area about 1 micron square. The grains appear to be roughly ellipsoidal, with a minor axis about 80 nm. and a major axis about 160 nm. The average grain size in the body of the film will be smaller than is seen on the surface.

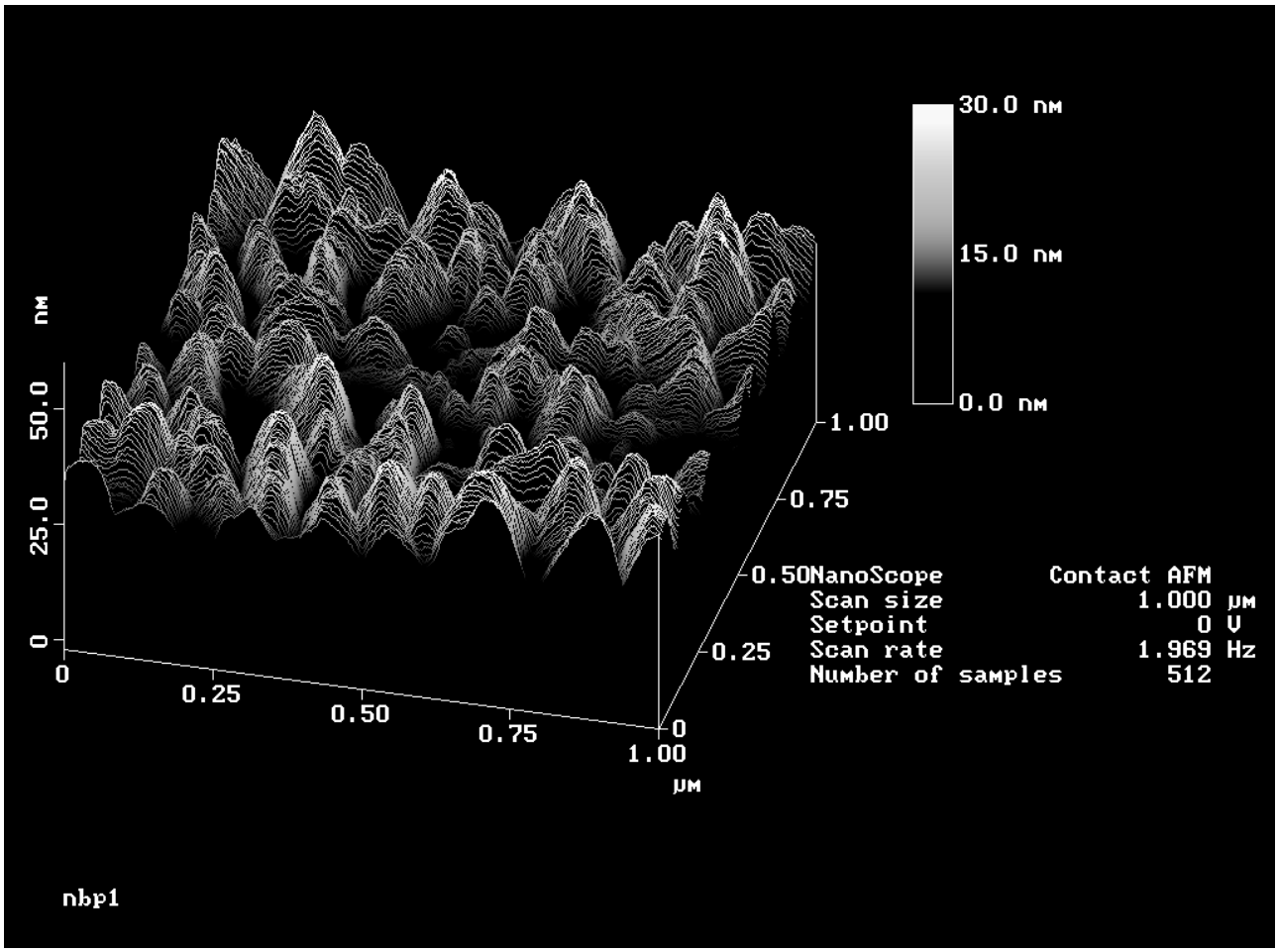

Figure 4. Contact AFM shows grain size on bare niobium surface of an uncapped film of the same batch as film "S".

5 REFERENCES

[1] *RF Superconductivity for Accelerators*, T. Hays, J. Knobloch and H. Padamsee, Wiley Series in Beam Physics and Accelerator Technology, John Wiley \& Sons, 1998.

[2] An excellent source is the published Proceedings of the biennial Workshops on RF Superconductivity, the most recent of which was held at Abano Therme, Italy in October 1997.

[3] B. Bonin and R.W. Roeth, Proc. of the 5th Workshop on RF Superconductivity, D. Proch Ed., Hamburg: DESY, 1991, p.210.

[4] C. Benvenuti, S. Calatroni et al., Paper presented at the Applied Superconductivity Conference, 1998. S. Calatroni gave a talk at Cornell to the SRF Group in September 1998.

[5] *Hydrogen in Metals III Properties and Applications*, H. Wipf, editor. Springer-Verlag 1997.

[6] Y.H. Kim, R.O. Suzuki, H. Numahura, H. Wada, and K. Ono, Journal of Alloys and Compounds **248**, p 251 (1997).

[7] "Advanced Thermometry Studies of Superconducting RF Cavities." Jens Knobloch 1997 CLNS THESIS 97-3, Cornell University, Ithaca New York.

[8] See for example, "Explosive Field Emitter Processing in Superconducting RF Cavities", J. Knobloch and H. Padamsee, *Particle Accelerators*, V61, pp.[443-468/169-204] (1998).

[9] "Improvement of Metals Technologies through Surface Analysis", N.S. McIntyre et al., SSW, Western Science Center, University of Western Ontario.

[10] "Dryerite" is a trade name for anhydrous calcium sulfate.

[11] "Hydrogen absorption and its effect on low-temperature electric properties of niobium", S. Isagawa, J. Appl. Phys. **51**(8)t, 4460, August 1980.

[12] "*Diffusion of titanium and niobium in BCC Ti-Nb alloys*", A.E. Ponteau and D. Lazars, Phys. Rev. B **19, 4027 (1979).**